

METHOD OF MAKING CATALYST FOR CARBON NANOTUBES AND  
CARBON NANOFIBERS AND CATALYST FOR CARBON NANOTUBES AND  
NANOFIBERS THEREOF

5 FIELD OF THE INVENTION

The present invention relates to a catalyst for carbon nanotubes and nanofibers and a method of making the same.

BACKGROUND ART

10 Carbon nanowires such as carbon nanotubes and carbon nanofibers are new utility materials excellent in electrical and mechanical properties. Generally, as a method of making the carbon nanowires, there are an arc-discharge method, a laser evaporation method, a vapor phase growth method, an electrolysis method, etc. The vapor phase growth method classified into a method using a substrate and a method using no-substrate, wherein the method of directly supplying a reaction gas and a catalyst without the substrate into a reactor is prefer 15 to massively synthesize the carbon nanowires.

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The catalyst used in the vapor phase growth method for the carbon nanowires is made by (1) oxidation and reduction (precipitation/coprecipitation) from various metal salts using ammonium bicarbonate, P.E.Anderson et.

evaporation/deposition of metallocene in a reducing ambient; (3) spraying/drying of pure metal dispersed in a solvent; (4) vacuum deposition of transition metal particles on the substrate containing alumina or silica; 5 etc. In the case of (2) and (3), there is needed a relatively expensive precursor. In the case of (1), the catalyst is directly made, so that a manufacturing process is complicated, an intermediate product causes pollution, and it is difficult to safekeep the catalyst 10 for a long time because the catalyst is likely to be oxidized again. In the case of (4), production cost of the catalyst is relatively high, and it is difficult to massively produce the catalyst.

#### DISCLOSURE OF INVENTION

15 Accordingly, it is an aspect of the present invention to provide a catalyst for carbon nanotubes and carbon nanofibers, and a method of making the same, in which production cost is reduced and it is possible to safekeep for a long time.

20 The foregoing and other aspects of the present invention are achieved by providing a method of making a catalyst for carbon nanotubes and nanofibers, comprising heating oxygen compound of transition metal in oxidative ambient at a temperature of 800°C through 1,500°C to be 25 transformed into an agglomerated transition metal oxide;

and powdering the agglomerated transition metal oxide into a minute particle.

According to another aspect of the present invention, the transition metal includes one or more selected from a group consisting of nickel (Ni), cobalt (Co), iron (Fe), molybdenum (Mo), and chrome (Cr).

According to another aspect of the present invention, the oxidation compound of the transition metal includes one or more selected from a group consisting of transition metal oxide, hydroxide, carbide, sulfide and nitride.

According to another aspect of the present invention, the agglomerated transition metal oxide is powdered to have an average particle size of 500 $\mu\text{m}$  or below.

According to another aspect of the present invention, the oxygen compound of the transition metal includes oxygen compound of copper.

According to another aspect of the present invention, the oxygen compound of copper ranges from 10% to 50% weight with regard to 100% weight of the transition metal oxide.

According to another aspect of the present invention, the oxygen compound of the transition metal is heated at a temperature of 800°C through 1,000°C.

According to another aspect of the present invention,

the oxygen compound of the transition metal is heated together with a support material selected from a group consisting of silica, alumina and magnesia.

According to another aspect of the present invention,  
5 the oxygen compound of the transition metal is heated at a temperature of 1,000°C through 1,400°C.

The foregoing and other aspects of the present invention are achieved by providing a catalyst for carbon nanotubes and nanofibers, which has an average particle 10 size of 500µm or below and in which transition metal oxide and copper oxide are sintered.

The foregoing and other aspects of the present invention are achieved by providing a catalyst for carbon nanotubes and nanofibers, which has an average particle 15 size of 500µm or below and in which transition metal oxide and a support material selected from a group consisting of silica, alumina and magnesia are sintered.

According to another aspect of the present invention, the transition metal includes one or more selected from a 20 group consisting of nickel (Ni), cobalt (Co), iron (Fe), molybdenum (Mo), and chrome (Cr).

#### MODES FOR CARRYING OUT THE INVENTION

Reference will now be made in detail to the embodiments of the present invention, examples of which 25 are illustrated in the accompanying drawings, wherein

like reference numerals refer to like elements throughout. The embodiments are described below in order to explain the present invention by referring to the figures.

According to an embodiment of the present invention,  
5 a catalyst made including a support material is mostly employed in manufacturing a carbon nanotube. On the other hand, a catalyst made including oxygen compound of copper without the support material is mostly employed in manufacturing a carbon nanofiber.

10 Hereinbelow, the catalyst for the carbon nanotube and the catalyst for the carbon nanofiber will be described separately.

First, a method of making the catalyst for the carbon nanotube includes the following three steps.

15 A first step: oxygen compound powder of one or more kinds of transition metal and support material powder of one or more selected among silica, alumina and magnesia are uniformly mixed.

A second step: the mixture is annealed in an  
20 oxidative ambient.

A third step: the annealed and agglomerated mixture is cooled and powdered by the micron scale.

In the case where the carbon nanotube is manufactured by a vapor phase growth method, and hydrogen  
25 gas in addition to carbon source gas is used as carrier

gas, there is not needed for reducing metal oxide into metal which is unstable in the atmosphere because reduction and carbon deposition reactions are performed at the same time by the catalyst according to an 5 embodiment of the present invention. Likewise, this is applied to the manufacturer of the carbon nanofiber.

In the first step, there is not limit to the particle size of the foregoing powders. However, the powder preferably has the micro scale size because the 10 powder is deteriorated in reactivity, uniformity, and heat transfer property according as the particle size thereof is increased. The oxygen compound of the transition metal includes the oxygen compounds of nickel, cobalt, iron, molybdenum and chrome, that is, includes 15 one or more selected among oxide, nitride, carbide, sulfide and hydroxide. The support material includes one or more selected among silica, alumina and magnesia. To uniformize distribution of the catalyst, the oxygen compound of the transition metal and the support material 20 are sufficiently mixed in a drum mixer or the like.

In the second step, the mixture is treated to have a briquette formation, or is being put in a crucible, and then heated at a temperature of 800 ~ 1,500°C in the oxidative ambient by inserting it in an electric furnace. 25 The oxidative ambient comprises atmosphere ambient.

Preferably, the oxidative ambient includes the atmosphere. At this time, a temperature of 1,000 ~ 1,400°C is preferable. Further, a temperature of 1,200°C ~ 1,300°C is more preferable. The heated mixture is calcined/annealed, 5 so that the oxygen compound of the transition metal is transformed into a transition metal oxide. While the oxygen compound of the transition metal is transformed into the transition metal oxide, the transition metal oxide and the support material are sintered, so that the 10 transition metal oxide and the support material are formatively mixed, thereby allowing a formative interface to be in a deposition state. If the mixture is heated at a temperature of 800°C or below, it takes so long time to calcine/anneal the mixture and it is difficult to get a 15 compact mixture formation. If the mixture is heated at a temperature of 1,500°C or more, it is softening-fused or coarsened. Meanwhile, a heating time is related to the amount of the mixture inserted in the electric furnace. Preferably, the mixture is sufficiently heated until the 20 whole mixture formation is uniform. In this case, the content of the transition metal oxide shows catalyst performance in a broad fraction of a whole mixture weight, and preferably ranges from 5% to 95%. If the content of the transition metal oxide is beyond the range from 5% to 25 95%, a yield is so low that it is not practical. Through

the second step, the mixture is sintered to have a agglomerated formation.

In the third step, the agglomerated mixture is powdered by the micron scale. Preferably, the 5 agglomerated mixture is cooled before being powdered.

On the other hand, a method of making the catalyst for the carbone nanofiber includes the following three steps.

A first step: there are provided oxygen compound of 10 one or more kinds of the transition metal. Preferably, the oxygen compound of copper is provided and mixed with the provided oxygen compound of the transition metal.

A second step: the mixture is annealed in the oxidative ambient.

15 A third step: the annealed and agglomerated mixture is cooled and powdered by the micron scale.

Contrary to the catalyst for the carbon nanotube, there is not needed the support material. Substitutively, the provided oxygen compound of the transition metal is 20 preferably sintered together with the oxygen compound of copper or the oxygen compound of other kinds of transition metal, thereby being formatively mixed. Further, in the second step, the mixture is annealed at a temperature of 800 ~ 1,000°C. Here, a heating time is in 25 proportion to the amount of the mixture. Preferably, the

mixture is sufficiently heated until the whole mixture formation is uniform. Then, the heated mixture is calcined/annealed, so that the oxygen compound of the transition metal and the oxygen compound of copper are 5 transformed into a transition metal oxide and a copper oxide. While the oxygen compound of the transition metal and the oxygen compound of copper is transformed into the transition metal oxide and the copper oxide, the transition metal oxide and the copper oxide are sintered, 10 so that the transition metal oxide and the copper oxide are formatively mixed, thereby allowing a formative interface to be in a deposition state. In the case of using the oxygen compound of copper, the content of the copper oxide shows catalyst performance in a broad 15 content range, and preferably ranges from 10% to 50% weight with regard to 100% weight of the transition metal oxide.

A carbon deposition test is performed using the catalyst powder made by the foregoing process. Test 20 results are good. Hereinbelow, the present invention will be described in more detail through the following embodiments, but is not limited to.

[embodiment 1]:  $\text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3$  catalyst

Hematite ( $\text{Fe}_2\text{O}_3$ ) powder and alumina ( $\text{Al}_2\text{O}_3$ ) powder are 25 mixed by a weight ratio of 1:1 in the drum mixer for

three hours. The mixed powder of 10g is put in an alumina container and then heated in the atmosphere at a temperature of 1,300°C in a box-type electric furnace for two hours. Then, the sintered mixture is cooled in the 5 furnace. The agglomerated mixture is taken out from the electric furnace and powdered by a micron meter of 100 or below.

This powder of 0.3g is put in an alumina boat, and then put in a pipe-type furnace mounted with a quartz 10 tube a diameter of 60mm. Then, the powder of 0.3g is heated in a nitrogen ambient at a temperature of 650°C, is treated with reduction and carbon depositing reaction for 40 minutes in the state that nitrogen is substituted by mixed gas of 0.1l/min hydrogen and 0.1l/min ethylene, and 15 is cooled to have a normal room temperature in the state that the mixed gas is substituted by nitrogen. After the cooling operation, a black material looking like the deposited carbon is observed by a transmission electron microscope. In result, a carbon nanotube of a hollow 20 shape having an average diameter of 10 ~ 50nm is observed.

Besides, in the cases where catalysts are made by the same method as used in the first embodiment, using Fe<sub>2</sub>O<sub>3</sub>-MgO in a weight ratio of 1:1, using Fe<sub>2</sub>O<sub>3</sub> -SiO<sub>2</sub> in a weight ratio of 1:1, using Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO in a weight

ratio of 1:0.5:0.5, using  $\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{MgO}$ - $\text{Al}_2\text{O}_3$  in a weight ratio of 1:0.5:0.5:0.5, using  $\text{NiO}$ - $\text{MgO}$  in a weight ratio of 1:1, using  $\text{CoO}$ - $\text{SiO}_2$  in a weight ratio of 1:1, using  $\text{Fe}_2\text{O}_3$ - $\text{NiO}$ - $\text{Al}_2\text{O}_3$  in a weight ratio of 1:1:1, and using 5  $\text{Fe}_2\text{O}_3$ - $\text{NiO}$ - $\text{CoO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{MgO}$  in a weight ratio of 1:1:1:1:1:1, respectively, carbon nanotubes of a hollow shape having an average diameter of 10 ~ 50nm are observed as results of the carbon depositing reaction, like the first embodiment.

10 [embodiment 2]:  $\text{Fe}_2\text{O}_3$  -  $\text{NiO}$  catalyst

Hematite ( $\text{Fe}_2\text{O}_3$ ) powder and nickel oxide ( $\text{NiO}$ ) powder are mixed by a weight ratio of 1:1 in the drum mixer for three hours. The mixed powder of 10g is put in an alumina container and then heated in the atmosphere at a 15 temperature of 900°C in the box-type electric furnace for two hours. Then, the sintered mixture is cooled in the furnace. The sintered mixture is taken out from the electric furnace and powdered by an average micron meter of 100 or below.

20 This powder of 0.3g is put in the alumina boat, and then put in the pipe-type furnace mounted with the quartz tube having a diameter of 60mm. Then, the powder of 0.3g is heated in the nitrogen ambient at a temperature of 550°C, is treated with reduction and carbon depositing

reaction for 40 minutes in the state that nitrogen is substituted by mixed gas of 1l/min hydrogen and 0.2l/min acetylene, and is cooled to have a normal room temperature in the state that the mixed gas is 5 substituted by nitrogen. After the cooling operation, a black material looking like the deposited carbon is observed by the transmission electron microscope. In result, a carbon nanofiber of a solid shape having an average diameter of 200nm is observed.

10 [embodiment 3]: NiO - CuO catalyst

Nickel oxide (NiO) powder and copper oxide (CuO) powder are mixed by a weight ratio of 7:3 in the drum mixer for three hours. The mixed powder of 10g is put in an alumina container and then heated in the atmosphere at 15 a temperature of 1,000°C in the box-type electric furnace for two hours. Then, the sintered mixture is cooled in the furnace. The sintered mixture is taken out from the electric furnace and powdered by an average micron meter of 100 or below.

20 This powder of 0.3g is put in the alumina boat, and then put in the pipe-type furnace mounted with the quartz tube having a diameter of 60mm. Then, the powder of 0.3g is heated in the nitrogen ambient at a temperature of 550° C, is treated with reduction and carbon depositing 25 reaction for 40 minutes in the state that nitrogen is

substituted by mixed gas of 1l/min hydrogen and 0.2l/min acetylene, and is cooled to have a normal room temperature in the state that the mixed gas is substituted by nitrogen. After the cooling operation, a 5 black material looking like the deposited carbon is observed by the transmission electron microscope. In result, a carbon nanofiber of a solid shape having an average diameter of 200nm is observed.

[comparative embodiment 1]:  $\text{Fe}_2\text{O}_3$  -  $\text{Al}_2\text{O}_3$  catalyst

10       Hematite ( $\text{Fe}_2\text{O}_3$ ) powder and alumina ( $\text{Al}_2\text{O}_3$ ) powder are mixed by a weight ratio of 1:1 in the drum mixer for three hours. The mixed powder of 0.3g is put in an alumina boat, and then put in the pipe-type furnace mounted with the quartz tube having a diameter of 60mm.

15       Then, the powder of 0.3g is heated in a nitrogen ambient at a temperature of 650°C, is treated with reduction and carbon depositing reaction for 40 minutes in the state that nitrogen is substituted by mixed gas of 1l/min hydrogen and 0.1l/min ethylene, and is cooled to have a 20 normal room temperature in the state that the mixed gas is substituted by nitrogen. After the cooling operation, the carbon nanotube or the carbon nonofiber is not observed. The reason why the carbon nanotube or the carbon nanofiber is not observed is that the transition 25 metal and the support material are not heated in the

oxidative ambient and therefore are not formatively mixed.

[comparative embodiment 2]: Ni - CuO catalyst

Nickel powder and copper oxide (CuO) powder are mixed by a weight ratio of 7:3 in the drum mixer for 5 three hours. The mixed powder of 0.3g is put in the alumina boat, and then put in the pipe-type furnace mounted with the quartz tube having a diameter of 60mm. Then, the powder of 0.3g is heated in the nitrogen ambient at a temperature of 550°C, is treated with 10 reduction and carbon depositing reaction for 40 minutes in the state that nitrogen is substituted by mixed gas of 1l/min hydrogen and 0.2l/min acetylene, and is cooled to have a normal room temperature in the state that the mixed gas is substituted by nitrogen. After the cooling 15 operation, the carbon nanofiber or the carbon nanotube is not observed. The reason why the carbon nanofiber or the carbon nanotube is not observed is that two catalyst materials are not heated in the oxidative ambient and therefore are not formatively mixed.

20 As described above, the present invention provides a catalyst for carbon nanowires, and a method of making the same, in which a catalyst for a massive and inexpensive carbon nanowires can be simply and inexpensively made.

Although a few embodiments of the present invention 25 have been shown and described, it will be appreciated by

those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims and their equivalents.